The CO_2 content of primitive bubble-bearing island-arc melt inclusions: a comparative study of Raman-spectroscopy of melt inclusion bubbles, mass-balance calculations and experimental homogenization of melt inclusions

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In the interest of constraining the volatile budgets of the Earth's interior, melt inclusions are a valuable tool because they provide a geologically persistent record of melt volatile contents before they degas to the atmosphere during volcanic eruptions. However, melt inclusions require special care because of the possibility for volatile elements to diffuse from the glass into a separate fluid phase (bubble; e.g. CO_2) or out of the olivine host (e.g. H_2O). For example, Mironov et al. (2015) recently demonstrated that it is possible to completely homogenize naturally dehydrated melt inclusions under high H_2O pressure and controlled fO_2 and redissolve all the CO_2 lost to vapor bubbles into the melt (glass). We used these experimental data and obtained CO_2 content in melt inclusions to test an alternative approach based on Raman spectroscopy of vapour bubbles and mass-balance calculations (following the methods described by Moore et al., 2015) to quantify bulk CO_2 contents of primitive arc melt inclusions from the same samples studied by Mironov et al. (2015).

The inclusions analysed come from two populations of olivine phenocrysts from the Klyuschevskoy volcano: 1) naturally quenched H_2O-rich inclusions from tephra samples, and 2) naturally-dehydrated H_2O-poor inclusions from lava samples, experimentally reheated and partially homogenized (melt+vapor bubbles) at 1 atm. We were able to quantify the density of CO_2 in 37/77 the natural inclusions and 11/20 of the reheated samples using Raman spectra. In general, the reheated inclusions tend to have larger bubbles (~3-10 vol%) than the natural inclusions (~1-5 vol%) and contain a lower density fluid (reheated: up to ~0.17 g/cc CO_2; natural: up to ~0.21 g/cc CO_2). Additionally, a carbonate peak is present in some of the Raman spectra of the natural inclusions, indicating that carbonate minerals are present on the surface of the bubble. Also, a secondary set of CO_2 peaks in the Raman spectra of the reheated inclusions suggests that CO_2 may be present as a liquid near the surface of the vapor bubble, so that the total density of the fluid in some of the reheated inclusions is significantly higher than the range given above. Although we have not analyzed the CO_2 content of the glass, it is possible to calculate minimum concentrations of CO_2 in the inclusions using mass balance calculations that ignore CO_2 in the glass. The amount of CO_2 stored in the bubbles corresponds to about 1400-2400 ppm for the natural inclusions and about 2300-4000 ppm for the reheated inclusions (interquartile range). Our minimum CO_2 contents for the reheated inclusions are in agreement with the results obtained by the rehydration method. Because we observed more CO_2 in the bubbles of reheated samples it is apparent that during dry reheating conditions, most of the CO_2 in the glass – and possibly some of the "CO_2" in carbonates – has likely diffused into the bubble. This suggests that the rehydration technique of Mironov et al. (2015) is an effective way to rehomogenize melt inclusions, and that dry reheating will remove CO_2 from the glass and carbonates and sequester them in fluid bubbles.

Finally, in order to compare CO_2 contents obtained using both independent approaches, we calculated bulk (glass + bubble) CO_2 concentrations using a range of analyses of melt inclusion glass from the naturally-quenched tephra samples (880-1200 ppm; Mironov et al., 2015), and the reheated lava samples (80-270 ppm; Mironov & Portnyagin, 2011). For both cases, we used the upper quartile value obtained from Raman analysis of bubbles to account for the effect of degassing. Restored CO2 concentrations are about 3280-3600 ppm for naturally-quenched melt inclusions and 4080-4270 ppm for reheated melt inclusions, which are in agreement with the range of 3600-4000 ppm reported by Mironov et al. (2015) using the experimental rehydration method.

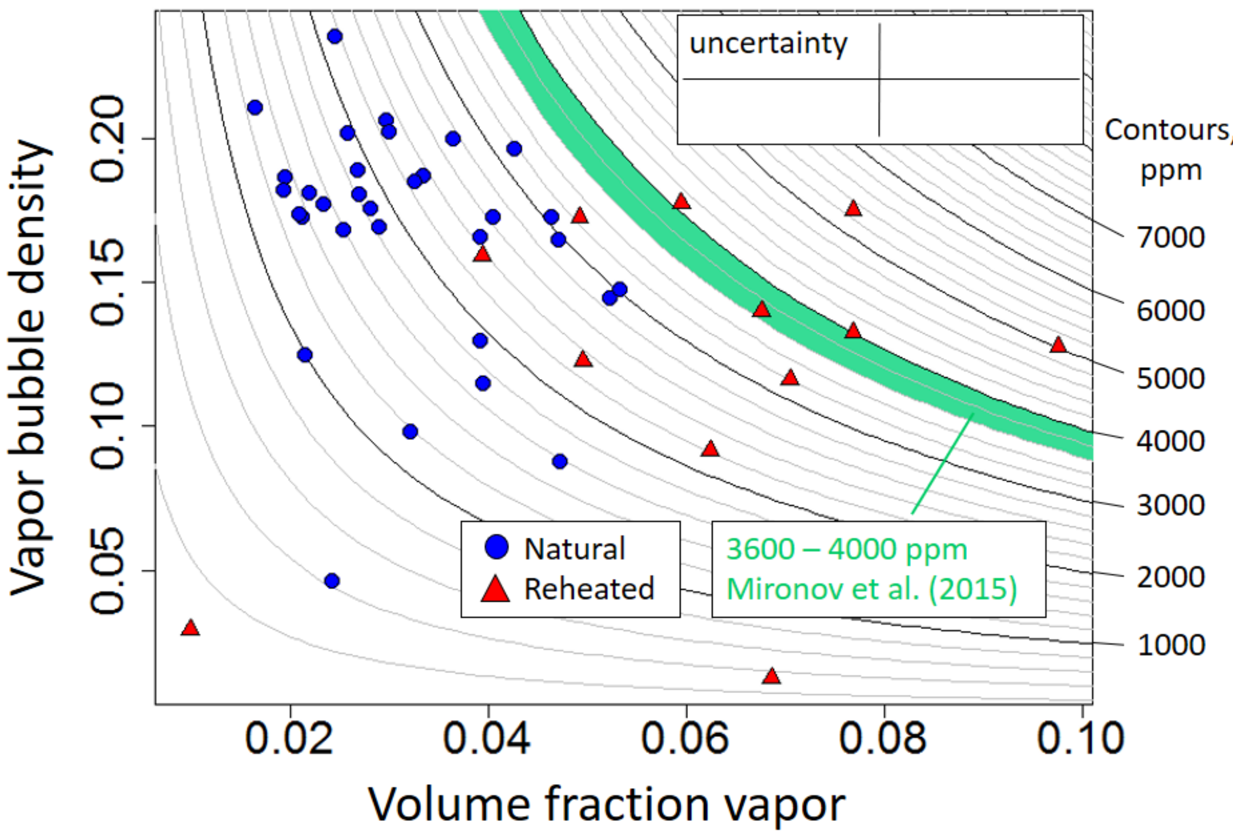

Figure 1: Results of Raman spectroscopic analyses of bubble-bearing melt inclusions from Klyuchevskoy Volcano. Circles and triangles represent naturally-quenched and reheated (dry + 1 atm) inclusions respectively. Contours represent the minimum CO_2 concentration for bubble-bearing inclusions as a function of bubble volume fraction and vapor density. The shaded region indicates uppermost CO_2 concentrations of rehydrated melt inclusion glasses and analyzed by Mironov et al. (2015). Uncertainties for vapor density and bubble volume fraction (2σ) are approximately ±0.02 g/cm^3 and ±0.02 (or 2 volume %) respectively.

REFERENCES

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